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THE ELECTRON SPIN RESONANCE SPECTRA AND STRUCTURES OF ORGANOTIN DERIVATIVES OF 3,6-DI-t-BUTYL-1,2-BENZOSEMIQUINONE

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Summary

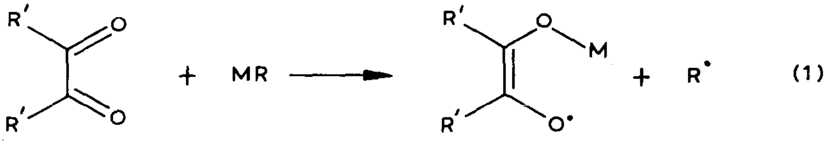
Organotin compounds react with 3,6-di-t-butyl-1,2-benzoquinone to give tin derivatives of the orthosemiquinone, $X_3SnOC_6H_2Bu^t_2O^{\cdot}$. The structures of these radicals have been investigated by ESR spectroscopy. When $X_3Sn = Cl_3Sn$, or RCl_2Sn, the spectrum shows hyperfine coupling to one unique chlorine atom at low temperature. It is concluded that the dione acts as a bidentate ligand about trigonal bipyramidal tin which carries apical and equatorial chloro ligands which are magnetically non-equivalent at low temperature, but undergo positional exchange as the temperature is raised.

When $X_3Sn = R_2ClSn$, the dione acts as a monodentate ligand, but the organotin group migrates between the two oxygen atoms at a rate commensurate with the ESR time scale, and the kinetics of the migration of the groups Me_2ClSn, Bu_2ClSn, Ph_2ClSn (and $(MeCO_2)_3Sn$ and Me_3ClPb)) have been determined. When $X_3Sn = R_3Sn$, the fluxionality is higher, and over the whole accessible range of temperature, the spectrum is that of a molecule with time-averaged C_{2v} symmetry.

Organolead compounds show the same broad pattern of behaviour.

Introduction

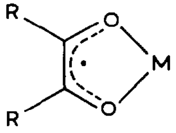
Numerous studies have been reported of the organometallic derivatives of semidiones. One aspect of the interest in these compounds is the potential use of the dione-organometallic system as a source of radicals R$^{\cdot}$ for initiating homolytic polymerisation [1].



(1)

A second is the use of diones as spin traps for organometallic radicals. Third, a great deal of attention has been paid to the structures of these derivatives [2]. They can in principle involve the dione as a monodentate static (I) or fluxional (I ⇌ II) ligand, or as a bidentate ligand (III), and, if the dione is acyclic (e.g. if it is biacetyl), *trans* modifications of structures I and II must also be considered; we were able to identify all these possible structures in the adducts formed between biacetyl and organotin radicals [2].

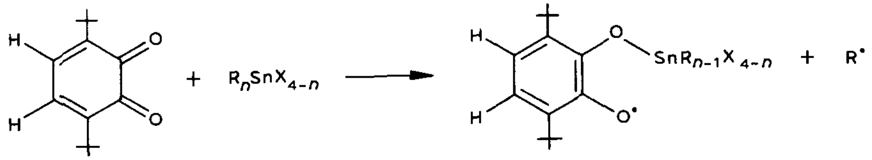
(I) (II)



(III)

These compounds are also closely related to the organometallic derivatives of the 1,2-diols, which are attracting attention because their special structural features render them suitable for use as organometallic "templates" in organic synthesis [3].

As an aid to identifying the adducts formed by various organotin radicals and 1,2-diones, we carried out an ESR study of the organotin derivatives IV of 3,6-di-t-butyl-1,2-benzosemiquinone, prepared by reaction 2, and the results are summarized here.



(2)

(IV)

This system has the advantage that the orthosemiquinone is stable, the radical adducts are easily prepared and are long-lived, complications from *trans* structures are absent, and the ESR spectra are simple but yet diverse enough to allow the different structures I, I ⇌ II, and III, to be distinguished.

Similar studies involving tin [4,5], as well as other metals, have been reported by Prokof'ev, Bubnov, Razuvaev, and their colleagues.

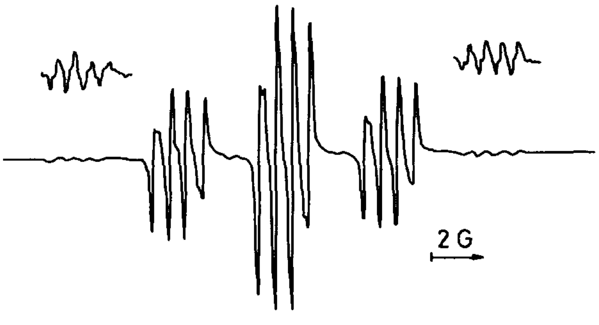


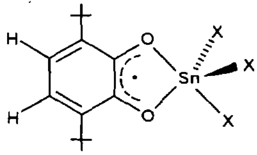
Fig. 1. Third derivative ESR spectrum of the radical V, $X_3 = Cl_3$, obtained from the reaction of $CpSnCl_3$ and 3,6-di-t-butyl-1,2-benzoquinone in toluene at 26°C, and showing partial resolution of the hyperfine coupling by the ^{35}Cl and ^{37}Cl, and the ^{117}Sn and ^{119}Sn isotopes.

Results and discussion

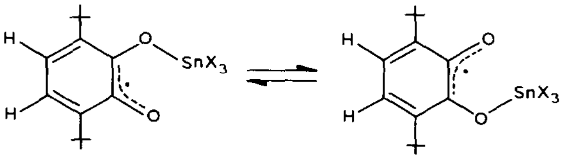
The ESR spectra of the organotin radicals prepared by reaction 2 are summarized in Table 1. The results imply a series of structures parallel to those which we identified for the adducts which the alkylchlorotin radicals form with biacetyl [2].

We consider first the adducts formed by the $^{\cdot}SnCl_3$ radical (Fig. 1). The hyperfine coupling by one unique chlorine atom at low temperature clearly indicates the presence of a 5-coordinate tin atom as shown in V ($X_3 = Cl_3$); with a unique apical chlorine ligand. Any non-equivalence between the aromatic protons is too small to be resolved.

The quartet coupling by one chlorine atom can be clearly resolved up to 26°C in toluene solvent, but then the resolution deteriorates. At 200°C, in molten naphthalene, coupling was apparent to all three chlorine atoms. The temperature at which the three chloro ligands become magnetically equivalent is therefore appreciably higher than with the corresponding biacetyl compound.



(V)



(VI) (VII)

The behaviour of the dialkyltin dichlorides, R_2SnCl_2, was more complicated. All three (R = Me, Bu, and Ph), showed the formation of two radicals, as illustrated in Fig. 2. The first radical showed hyperfine coupling to one chlorine atom, similar to that described for ($X_3 = Cl_3$), but hyperfine coupling to tin could not be detected, the g value was lower, and the two chloro ligands became equivalent at a lower temperature (below −10°C). We identify this as the radical V ($X_3 = R_{eq}$, Cl_{eq}, Cl_{ap}) in which positional exchange of the ligands occurs at the higher temperatures.

The characteristics of the second radical (^1H and ^{119}Sn hyperfine coupling constants, temperature dependence, and g value) were identical with those for the radical VI ($X_3 = R_2Cl$) described below. It appears therefore that the reaction of dialkyltin dichlorides can involve not only the loss of an alkyl radical as shown in equation 2, but also the loss of a chlorine atom.

Reaction of the quinone with trialkyltin chlorides proceeded cleanly by reaction 2. At low temperature the ESR spectrum showed hyperfine coupling to two non-equivalent protons. As the temperature was increased, the central pair of lines broadened and then collapsed to a singlet. Our results for the reaction of trimethyltin chloride are similar to those in the literature [4]. The kinetics of the exchange were determined by computer simulation of the spectra through the region of intermediate rates of exchange (see Fig. 3), and the results are given in Table 2.

These reactions can be regarded as degenerate S_H2 reactions by an aryloxyl radical at a tin centre, where the reactants and products have the structure VI ($X_3 = R_2Cl$) and the transition state or intermediate has the structure V ($X_3 = R_2Cl$). The reduction in rate in going from the methyl to the butyl derivative may result from steric compression in V, when R = butyl. Replacing the butyl groups by phenyl groups causes compensating changes in the pre-exponential factor and the activation energy so that the rate constant at 293 K is little affected.

(Continued on p. 58)

TABLE 1

ESR SPECTRA OF ORGANOTIN DERIVATIVES OF 2,6-DI-t-BUTYL-1,2-BENZOSEMIQUINONE (IV)

Reagent	$R_{n-1}SnX_{4-n}$	solvent [a]	T (°)	a (G)			g	Notes
Me_6Sn_2	Me_3Sn	T	0	3.6(2H)		13.0(Sn)		*b*
Bu_4Sn, Bu_6Sn_2	Bu_3Sn	T	−10	3.6(2H)		13.6(Sn)	2.0036	*c*
Bu_3SnCp								
$Bu_3SnC_3F_7$	$Bu_2SnC_3F_7$	T	−35	2.9(1H)	4.0(1H)		2.0037	
			+68	3.4(1H)	4.1(1H)			
Cp_4Sn	Cp_3Sn	T	−50	3.8(2H)		7.4(Sn)	2.0033	*d*
Ph_4Sn	Ph_3Sn	T	−10	3.7(2H)		12.0(Sn)	2.0030	*e*
Ph_3SnCp								
Me_3SnCl	Me_2SnCl	X	−65	2.5(1H)	5.0(1H)	22.3(Sn)	2.0037	*f*
			+131	3.7(2H)		19.2(Sn)		
Bu_3SnCl	Bu_2SnCl	T	−14	2.6(1H)	4.9(1H)	25.2(Sn)	2.0037	*d*
$Bu_2SnCpCl$			+104	3.6(2H)				
Ph_3SnCl	Ph_2SnCl	X	−44	2.8(1H)	4.8(1H)	17.5(Sn)	2.0037	
			+138	3.7(2H)		15.8(Sn)		
Me_3SnOAc	Me_2SnOAc	T	−66	2.4(1H)	5.0(1H)	20.2(Sn)	2.0056	
			+94	3.6(2H)		17.8(Sn)		
Bu_3SnOAc	Bu_2SnOAc	T	−44	2.5(1H)	4.9(1)	22.8(Sn)	2.0041	*g*
Bu_3SnF	Bu_2SnF	T	−53	2.5(1H)	4.8(1H)	23.0(Sn)	2.0041	
			−64	3.4(1H)	3.9(1H)	1.0(IF)		

Me_2SnCl_2	$MeSnCl_2$	T	−50	3.8(2H)	0.6(Cl)			
Bu_2SnCl_2	$BuSnCl_2$	T	−26	ca. 4.4(2H)	0.6(Cl)			
	Bu_2SnCl	T		4.9(1H)	2.6(1H)			
Ph_2SnCl_2	$PhSnCl_2$	T	−52	3.9(2H)	0.6(1Cl)		2.0029	
			16	3.9(2H)	0.45(2Cl)			
	Ph_2SnCl		−52	2.8(1H)	4.75(1H)	17.3(Sn)		
			103	3.8(2H)		15.8(Sn)		
$Bu_2Sn(OCOMe)_2$	$BuSn(OCOMe)_2$	T	−68	2.5(1H)	4.0(1H)	22.6(Sn)		g
			+23	7.3(1H)		22.2(Sn)		
$MeSnCl_3$	$SnCl_3$	T	−48	3.9(2H)	0.63(1Cl)	10.2(Sn)	2.0033	
		N	+200	3.8(2H)	0.5(3Cl)			
$BuSnCl_3$	$SnCl_3$	T	−56	4.0(2H)		10.4(Sn)	2.0033	
			−27	4.0(2H)	0.65(1Cl)	9.8(Sn)		
$CpSnCl_3$	$SnCl_3$	T	−71	4.0(2H)	0.63(1Cl)	11.0(Sn)	2.0033	d
			+26	4.0(2H)	0.63(1Cl)	7.5(Sn)		
$BuSn(OCOMe)_3$	$Sn(OCOMe)_3$	T	−52	3.2(1H)	4.4(1H)	4.2(Sn)	2.0033	
			+26	3.8(2H)		2.2(Sn)		
$CpSn(OCOEt)_3$	$Sn(OCOEt)_3$	T	−60	4.3(1H)	3.4(1H)	10.3(Sn)	2.0034	
			+21	3.9(2)		8.0(Sn)		

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[a] Solvents: T = toluene, X = xylene, N = naphthalene. [b] The same radical has been reported from the reaction of Me_4Sn, a(2H) 3.6 G, $a(^{119}Sn)$ 13.3 G [4]. Under the same conditions, Et_6Sn_2 gave the radical ($MX_3 = SnEt_3$), a(2H) 3.4 G, $a(^{119}Sn)$ 12.4 G [5]. [c] Also obtained by abstraction of H from the monotributyltin derivative of the diol [6]. [d] Ref. 6. [e] Ref. 5 gives a(2H) 3.6 G, $a(^{119}Sn)$ 11.6 G. [f] Ref. 4 gives a(1H) 2.6 G, a(1H) 5.2 G at −70°C, and a(2H) 3.6 G, $a(^{119}Sn)$ 22.9 G at +110°C. [g] The radical decomposed before the region of fast exchange could be reached.

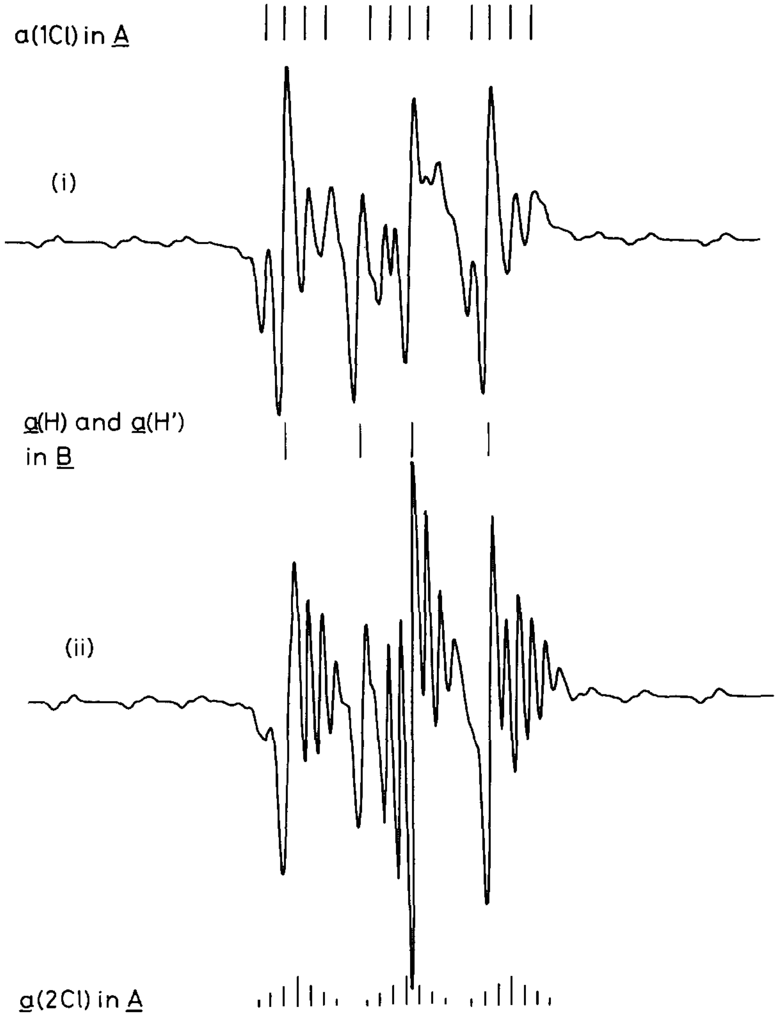

Fig. 2. First derivative ESR spectra of the radicals V and VI, $SnX_3 = PhSnCl_2$ (A) and Ph_2SnCl (B), obtained from the reaction of Ph_2SnCl_2 with 3,6-di-t-butyl-1,2-benzoquinone in toluene. (i) At, −52°C. Radical A shows quartet coupling from one chlorine atom, and radical B shows a doublet of doublets from coupling with two non-equivalent ring protons. (ii) At +16°C. Radical A now shows septet coupling from two equivalent chlorine atoms, and the central pair of lines of B are beginning to broaden.

Returning to Table 1, the equivalence of the two aromatic protons in the products IV where SnX_3 is Me_3Sn, Bu_3Sn, or Ph_3Sn, must indicate that the semiquinone group is monodentate and fluxional (VI $\rightleftharpoons$ VII), since the tin would be less prone to increase its coordination than when the ligands are R_2Cl.

When one of the three butyl groups is replaced by C_3F_7, the increased electronegativity reduces the fluxionality, and the non-equivalence of the aromatic protons indicates that the complex has the static structure VI up to at least 68°C. The cyclopentadienyl group is more electronegative than a saturated alkyl group and might similarly be expected to reduce the fluxionality [6], but the spectrum of the Cp_3Sn complex showed that the aromatic protons were magnetically equivalent at

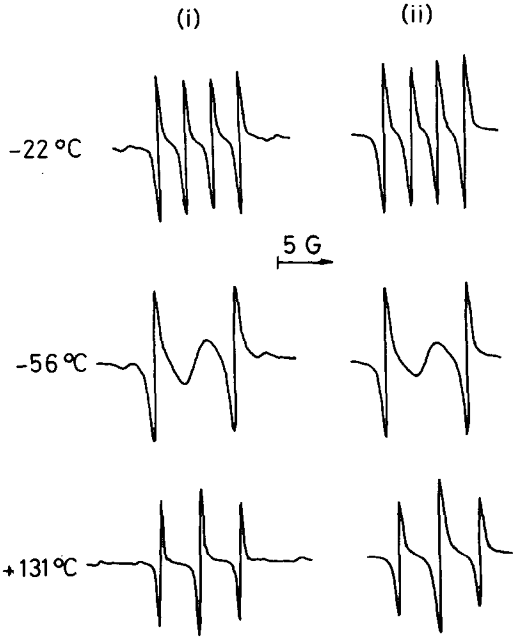

Fig. 3. First derivative ESR spectra (i), and computer simulations (ii) of the fluxional system VI ⇌ VII (X_3 = Me_2SnCl).

−50°C. This implies that the structure is either still rapidly fluxional like the trialkyltin complexes or fully 5-coordinate like the trichlorotin complex, and indeed the ^{119}Sn hyperfine coupling constant does have a low value, which seems to be associated with structure V.

As expected, the result of progressively replacing alkyl groups in R_3Sn by carboxylate ligands is similar to, but less pronounced than the effect of introducing chloro ligands: the mobility of the tin moiety is reduced, but even with three carboxylato groups, the spectra at low temperature clearly show that the semi-

TABLE 2

KINETIC PARAMETERS FOR THE METALLOTROPIC REARRANGEMENT OF ORGANOMETALLIC DERIVATIVES OF 3,6-DI-t-BUTYL-1,2-BENZOSEMIQUINONE AT 293 K

MX_3	Solvent [a]	Log A	E (kJ mol^{-1})	k (s^{-1})
Me_2ClSn	X	14.1	43.5	2.2×10^{6} [b]
Bu_2ClSn	T	13.6	44.4	4.7×10^{5} [c]
Ph_2ClSn	X	14.4	48.8	4.9×10^{5}
$(MeCO_2)_3Sn$	T	14.1	37.4	2.5×10^{7}
Me_2PbCl	T	11.7	28.2	4.6×10^{6}

[a] Solvents: T = toluene, X = xylene. [b] Ref. 4 reports log A 14.4 s^{-1}, E 44.9 kJ mol^{-1}, k 2.4×10^{6} s^{-1} at 293 K in toluene. [c] Ref. 6.

TABLE 3

ESR SPECTRA OF ORGANOLEAD DERIVATIVES OF 2,6-DI-t-BUTYL-1,2-BENZOSEMIQUINONE

Reagent	$R_{n-1}PbX_{4-n}$	Solvent [a]	T(°C)	a(G)			g
Me_3PbCp	Me_3Pb	T	−42	3.4(2H)		6.3(Pb)	2.0044
Ph_3PbCp	Ph_3Pb	T	−40	3.0(2H)		3.0(Pb)	2.0038 [b]
Ph_2PbCp_2	Ph_2CpPb	T	−41	2.7(1H)	4.3(1H)	2.5(Pb)	2.0035
			+64	2.7(1H)	4.3(1H)	3.0(Pb)	2.0036 [b]
Me_3PbCl	Me_2PbCl	X	+35	2.7(1H)	4.4(1H)	13.0(Pb)	
			+117	3.6(2H)		11.9(Pb)	
Ph_2PbCl_2	$PhPbCl_2$	T	+16	2.1(1H	−4.3(1H)	4.8(Pb)	2.0028
				7.3(1H)		4.2(Pb)	

[a] Solvents: T = toluene, X = xylene. [b] The spectrum shows an alternating line-width effect.

quinone is still acting as a monodentate rather than a bidentate ligand, and, as Table 2 shows, its mobility is greater than that of the group R_2SnCl. The comparison however may be complicated by the fact that the carboxylato ligands themselves may be bidentate *.

A few organolead compounds [7] were investigated for the purposes of comparison; the ESR spectra are listed in Table 3, and the one kinetic result is included in Table 2. The results parallel those obtained with the organotin compounds, and it will be noted that (1) R_3Pb complexes appear to carry monodentate semidione ligands that are fluxional down to low temperatures, and (2) the introduction of one chloro or one cyclopentadienyl ligand is sufficient to reduce the fluxionality so that it is commensurate with the ESR time scale. The one kinetic result suggests that the fluxionality of the tin and the lead derivatives is similar when the metals carry similar substituents.

Conclusion

The pattern of properties which emerges for the semiquinone complexes is thus similar to that established for the semidione complexes [2]. The trialkyltin derivatives are fast-fluxional, but the introduction of electronegative ligands such as Cl first reduces their fluxionality so that it becomes commensurate with the ESR time scale, and then it causes the dione to act as a bidentate ligands about 5-coordinate tin in which the three other ligands are divided into non-equivalent sets, X_2 and X'.

Experimental

ESR spectra were recorded using a Varian E4 spectrometer as described previously [6]. Third derivative displays of the spectra were obtained using a Telmore subharmonic generator.

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* Photolysis of cyclopentadienyltin triacetate in the presence of biacetyl at 80°C showed the ESR spectrum of the *cis* and *trans* $H^{\cdot}$ adducts, a(6H) 9.0 G, and a(3H) 14.0 G, a(3H) 2.5 G, respectively, rather than of any $^{\cdot}Sn(OCOMe)_3$ adduct.

Acknowledgements

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